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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the manufacturing method of the foam which makes it possible to manufacture easily the foam which has the air bubbles of a small path especially about the manufacturing method of foam used for a various application.

[0002]

[Description of the Prior Art]Conventionally, various methods are proposed as a manufacturing method of foam. For example, the manufacturing method of general foam is shown in JP,57-197132,A or JP,3-18817,B.

In these advanced technology, a heat decomposition type blowing agent is mixed to resin, heating is made to decompose a heat decomposition type blowing agent, gas is generated, and air bubbles are formed of it.

[0003]However, in the foam obtained by the method given in the advanced technology mentioned above, the range of a cell diameter is about 0.1-1.0 mm, and it was not able to form a smaller cell diameter, for example, about 1-10-micrometer air bubbles.

[0004]On the other hand, in JP,4-356540,A or the Patent Publication Heisei No. 506724 [ six to ] gazette, the manufacturing method of the foam which has the air bubbles of a smaller path is proposed in recent years.

[0005]That is, the method of making unreactive gas contain under application of pressure, and making it foam under pressureless into thermoplastics in the very narrow temperature requirement between the crystallization temperature of resin and the melting point is indicated by JP,4-356540,A. According to this method, it is supposed that the foam which has air bubbles with a cell diameter of about 8-30 micrometers will be obtained. A supercritical fluid is pressed fit and dissolved at resin, the temperature is lowered, with a pressure held, and resin

is cooled in the Patent Publication Heisei No. 506724 [ six to ] gazette, a pressure is wide opened in it, temperature is raised to it still more rapidly, and the method of making it foam by destabilizing an injected liquid (foaming agent) thermodynamically is indicated. Here, it is supposed that the foam which has air bubbles with a diameter of about 0.1-10 micrometers will be obtained.

[0006]However, by the method of the indication, resin had to be certainly held under pressureless in the very narrow temperature requirement between crystallization temperature and the melting point at JP,4-356540,A. Therefore, in order to have to control and optimize the mobility of a die temperature and resin, the pressure of resin, etc. with high precision, this method was not suitable for a mass production.

[0007]Although foaming arose by thermodynamic destabilization, the pressure and temperature of resin had to be finely controlled by the method of the indication in the Patent Publication Heisei No. 506724 [ six to ] gazette. In addition, in order to have produced continuously, there was also a problem of needing many expensive equipment, such as equipment for holding a pressure.

[0008]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the manufacturing method of the foam which cancels the fault of the conventional technology mentioned above, and makes it possible to manufacture the foam which has the air bubbles of a detailed path with easy equipment, and is suitable also for the mass production.

[0009]

[Means for Solving the Problem]It decomposes by irradiating radiation and the invention according to claim 1 irradiates with radiation a mixture obtained by mixing to resin a foaming agent which generates gas, is a manufacturing method of foam foaming to this resin, and attains a technical problem mentioned above by the above-mentioned process.

[0010]The invention according to claim 2 is a manufacturing method of foam which makes resin distribute a foaming agent and is made to foam to this resin on condition of predetermined, A foam formation generating agent which decomposes into resin in which a foaming agent was distributed by irradiating radiation, and makes it generate gas is mixed beforehand, and before making said resin foam, it is a manufacturing method of a foaming agent irradiating resin with radiation, and a technical problem mentioned above by the above-mentioned process is attained.

[0011]In attaining an aforementioned problem, it decomposes by irradiating radiation, and an invention given in claims 1 and 2 is common in having used an ingredient which generates gas.

[0012]Hereafter, details of an invention of a statement are explained to claims 1 and 2.

As the above-mentioned resin which can be used for resin this invention (invention given in claims 1 and 2) which can be used for an invention of a statement, arbitrary things can be used for claims 1 and 2 among resin which may be made to foam generally. As such resin, for example Polyethylene, polypropylene, or polybutene, Or an ethylene-vinylacetate copolymer, ethylene propylene rubber, Olefin system resin containing copolymers, such as an ethylene-(meta) acrylic acid copolymer; Vinyl chloride resin, VCM/PVC system resin, such as chlorinated polyethylene and VCM/PVC (meta) acrylic acid resin; Polystyrene, Poly alpha-methylstyrene, chlorination polystyrene, a styrene (meta) acrylic resin, Styrene resin, such as acrylonitrile-butadiene-styrene copolymer resin (henceforth, ABS plastics); An acrylic resin, Acrylic resin containing methacrylic resin and copolymerization resin with various acrylic ester; An ether system and an ester system, Thermoplastic urethane resin, such as a carbonate system; Amide system resin; polyethylene terephthalate, such as 6-nylon and 6,6-nylon, Saturation ester system resin, such as polybutylene terephthalate; Polycarbonate, Thermoplastics, such as polyether sulphone, polyether imide, a polyether ether ketone, liquid crystal resin, and fluororesin; Urethane resin by 2 liquid reactions of polyol and polyisocyanate, isocyanurate resin, amide resin, Thermosetting resin, such as imide resin, an epoxy resin, a urea resin, melamine resin, phenol resin, and unsaturation ester resin, may be mentioned, and these may be used alone, or two or more sorts may be mixed and used.

[0013]As the above-mentioned foaming agent which can be used in an invention of detailed claim 1 of the invention according to claim 1, it can be excited with radiation, and can decompose and arbitrary compounds which generate gas can be used. For example, as a foaming agent which generates nitrogen gas, 4-bromobenzene diazonium tetrafluoroborate, 4-chlorobenzene diazonium hexafluorophosphate, Diazo benzenoid compounds, such as 4-nitrobenzene diazonium hexafluorophosphate, 4-nitrobenzene diazonium tetrafluoroborate, a Fast Yellow GC salt, and DiazoRed RC, are mentioned. As what can mention alkaline-earth-metals hydrides, such as a magnesium hydride, a calcium hydride, and a barium hydride, and generates carbon monoxide as what generates hydrogen, Ketone compounds, such as dipropyl ketone, dibutyl ketone, propyl butyl ketone, cyclopentanone, and cyclohexanone, can be mentioned. In addition, by [ -- butane is mentioned as what generates carbon monoxide and methane as a thing which acetic acid 4-methyl phenol makes generate a butene and hydrogen gas -- ] irradiating with radiation, Ordinary temperature, such as nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen, methane, and ethane, is [ anything which generates gas with high steam pressure ] available.

[0014]In order to obtain air bubbles of the target path, after checking a distributed situation of resin and a foaming agent beforehand, it is preferred to determine a kind and an addition of a foaming agent. As a range with a preferred foaming agent addition, although based also on expansion ratio, it is 0.5 to 10 weight section still more preferably 0.1 to 20 weight section to

the resin 100 above-mentioned weight section. When less than 0.1 weight sections, expansion ratio is low, and if 20 weight sections are exceeded, a cell diameter will become large too much. It is as follows when a concrete example is given.

[0015]What is necessary is to add 4-bromobenzene diazonium tetrafluoroborate 2.5 weight section, and just to distribute resin uniformly to resin 100 weight section, in introducing air bubbles with a diameter of 1 micrometer into polyethylene and increasing expansion ratio 5 times.

[0016]What is necessary is to add propyl butyl ketone 0.6 weight section, and just to distribute resin uniformly to resin 100 weight section, in introducing air bubbles with a diameter of 0.5 micrometer into polycarbonate and increasing expansion ratio 1.5 times.

[0017]When resin has softened timing into which a foaming agent is made to disassemble, in the case of reactive resin like urethane, it is after the time of becoming the temperature more than the melting point in crystalline polymer after the time of becoming the temperature more than glass transition temperature in amorphous resin from a start of hardening to the completion of hardening. In order not to dissolve emitted gas in resin, to disassemble a foaming agent by a high pressure state, it is required to open a pressure wide and to foam to it promptly, so that emitted gas may not dissolve in resin. When disassembling a foaming agent by a room temperature condition, what is necessary is cautious only of the above-mentioned temperature conditions.

[0018]About combination of resin and a foaming agent, things with a near solubility parameter are preferred. However, it is preferred to add [ various ] a foaming agent at resin using a making machine to be used, and to examine a decomposing condition beforehand in selection of a foaming agent (temperature, position, etc.).

[0019]Direct dissociation of the above-mentioned foaming agent may be carried out with radiation, and in what cannot excite a foaming agent directly with a light source used, it may add a photosensitizer and may use energy transfer.

[0020]As mentioned above, by irradiating radiation, a foam formation generating agent used for details claim 2 of the invention according to claim 2 by invention of a statement is excited, and it decomposes and it generates gas. As such a foam formation generating agent, the same thing as the above-mentioned foaming agent used by the invention according to claim 1 can be used.

[0021]In order to obtain foam formation of the target path, after checking a distributed situation of resin and a foam formation generating agent beforehand, it is preferred to determine a kind and an addition of the above-mentioned foam formation generating agent. It is preferred to consider it as 0.01 to 1 weight section to the resin 100 above-mentioned weight section as a range with a preferred foam formation generating agent addition, and it is 0.05 to 0.5 weight section more preferably. In less than 0.01 weight sections, if generating of air bubbles does not

take place easily and one weight section is exceeded, a size of air bubbles will become large beyond generating of air bubbles, and gassing efficiency will fall. It is as follows when a concrete example is given.

[0022]What is necessary is to add 4-bromobenzene diazonium tetrafluoroborate 0.1 weight section, to distribute resin uniformly to resin 100 weight section, to irradiate with radiation at a metallic mold exit, and just to carry out the usual foaming after that, when introducing air bubbles with a diameter of 1 micrometer into polyethylene and making expansion ratio into 30 times.

[0023]What is necessary is to add propyl butyl ketone 0.15 weight section, to distribute resin uniformly to resin 100 weight section, to irradiate with radiation at a metallic mold exit, and just to carry out the usual foaming after that, in introducing air bubbles with a diameter of 0.5 micrometer into polycarbonate and making expansion ratio into 5 times.

[0024]It is the temperature more than glass transition temperature, and what is necessary is for timing into which a foam formation generating agent is made to decompose to be the temperature more than the melting point, and just to perform it with amorphous resin with crystalline polymer, from a time of hardening beginning in the case of reactive resin like urethane before the completion of hardening, when resin has become soft. In order to prevent emitted gas from dissolving in resin, to decompose a foam formation generating agent by a high pressure state, it is required to make it become the conditions which all of gas which completed predetermined foaming promptly after gassing, or was emitted do not dissolve in resin. In decomposing a foam formation generating agent in the state of ordinary pressure, what is necessary is careful only of the above-mentioned temperature conditions.

[0025]About combination of resin and the above-mentioned foam formation generating agent, things with a near solubility parameter are preferred. However, it is preferred to add [ various ] a foam formation generating agent at resin using a making machine to be used, and to examine decomposing conditions (temperature, a position, etc.) beforehand in selection of a foam formation generating agent.

[0026]Direct dissociation of the above-mentioned foam formation generating agent may be carried out with radiation, and although it cannot excite a direct foam formation generating agent with a light source used, it may add a photosensitizer to a case and may use energy transfer for it.

[0027]If it is used as a foaming agent used by the invention according to claim 2 in order to make resin foam, arbitrary things can be used, and optimal thing is chosen with combination with resin to which this foaming agent is made to foam. AZOJI carvone amide of azo as a heat decomposition type blowing agent as a typical foaming agent. A sulfo- nil semicarbazide system of (the following, ADCA), barium dicarboxylate, and a hydrazide system, etc., They are mentioned by inorganic system foaming agents, such as sodium bicarbonate, ammonium

carbonate, and ammonium acid carbonate, and as a physics type foaming agent, Hydrocarbon system compounds, such as butane, pentane, and cyclohexane, HCFC141b, Activated gas and these mixed gas, such as inactive gas, such as fluorinated hydrocarbon system compounds, such as HCFC142b and HFC134a, nitrogen, carbon dioxide, argon, or neon, oxygen, or hydrogen, are mentioned. When resin consists of thermosetting urethane resin, isocyanurate resin, amide resin, imide resin, etc., a chemical reaction type foaming agent, for example, carbon dioxide by which it is generated from a reaction of an isocyanate and water, may be used as a foaming agent. The above-mentioned foaming agent may be used independently, or may use two or more sorts together.

[0028]An addition of a foaming agent is determined by a relation with expansion ratio. What is necessary is just to add 15 weight sections of AZOJI carvone amide to resin 100 weight section in a heat decomposition type blowing agent, when it is simply determined with generating gas volume to resin, for example, makes it one 30 times the expansion ratio of this using AZOJI carvone amide. What is necessary is in the case of a physics type foaming agent, just to dissolve carbon dioxide by a pressure of  $80 \text{ kg/cm}^2$  to resin, in solubility to resin of a foaming agent being restrained, for example, making polyethylene foam to carbon dioxide as a foaming agent and making expansion ratio into 30 times. When using a chemical reaction type foaming agent, near expansion ratio is determined by quantity of water to add, but since it may be accompanied by reaction with resin, or a reaction with water or others, to inquire a priori is required.

[0029]With radiation in an invention of radiation claims 1 and 2, an electron beam, ultraviolet rays, visible light, etc. shall be included widely. An electron beam is obtained by using various acceleration machines or disassembly of a radioactive element, ultraviolet rays are generated from a high-pressure mercury-vapor lamp, a metal halide lamp, etc., and visible light is generated from laser, such as helium and argon. Although chosen according to a foam formation generating agent by invention of a foaming agent and claim 2 by the invention of claim 1, when it is chosen also with resin to which it foams, for example, carries out melting of the resin before foaming, ultraviolet rays and visible light may be unable to be used for a kind of these radiation depending on a presentation of resin.

[0030]In an invention of other ingredient claims 1 and 2 which can be added, In foam, besides material mentioned above, metallic oxides, such as glass fiber, titanium oxide, or magnesium oxide, A nucleating additive, a bulking agent, an antioxidant, colorant, foaming auxiliaries, etc., such as carbonate, such as magnesium carbonate or calcium carbonate, can be arbitrarily added, unless the purpose of this invention is checked.

[0031]It is not limited in particular for a concrete process of a manufacturing method of an invention of a statement to concrete process claim 1 of a manufacturing method of the invention according to claim 1. That is, a general method of manufacturing a resin-molding

article which contains air bubbles for usual foam or a weight saving can be used suitably. As a typical manufacturing method, the following \*\* extrusion-foaming methods, the \*\* bead foaming method, the \*\* chemical reaction foaming method, the \*\* SERUKA foaming method, the \*\* ejection foaming method, etc. can be mentioned.

[0032]\*\* Use an extrusion-foaming device shown in extrusion-foaming method drawing 1. This extrusion-foaming device attaches the metallic mold 2 which has the radiation irradiation window 2a which becomes the twin screw extruder 1 from sapphire glass, from a metallic mold tip, extrudes foam and fabricates it directly.

[0033]If it explains concretely, resin made to foam in the hopper 4 of the twin screw extruder 1 and a foaming agent, for example, 4-bromobenzene diazonium tetrafluoroborate, will be thrown in, and melt kneading of these will be carried out. In a tip part of the metallic mold 2 adjusted by temperature suitable for foaming, it lets the radiation irradiation window 2a pass, and irradiating with light of a high-pressure mercury-vapor lamp (80W), resin is extruded and is made to foam from a tip part of the metallic mold 2. Here, although a dose of radiation is rationalized by a light source and pass time of resin, a light source is usually selected so that it may end with irradiation time for about several seconds.

[0034]\*\* The bead foaming method this gentleman method is used abundantly obtaining foam of polystyrene. Melt kneading of polystyrene and a foaming agent, for example, the dibutyl ketone, is carried out with the twin screw extruder 1 as shown in drawing 1, and it fabricates in bead shape.

[0035]Next, heat foaming is carried out with a steam by making an obtained bead into a pre-expansion process, it irradiates with an electron beam, gasification of a foaming agent is caused, and predetermined foamed beads are manufactured. After replacing gas in air bubbles by air by the aging process, a bead is introduced into a predetermined metallic mold, heat foaming is carried out with a steam, and mold goods are obtained.

[0036]\*\* The chemical reaction foaming method this gentleman method is used as a typical process of foam of thermosetting urethane resin. It irradiates with an electron beam, gasification of a foaming agent is caused, and foam is fabricated at the same time mix beforehand a catalyst, polyol, and a foaming agent, for example, a magnesium hydride, next it mixes polyisocyanate, it introduces on a predetermined mold or a belt and a hardening reaction occurs.

[0037]\*\* The SERUKA foaming method this gentleman method is a method used as a weight saving method of rigid resin. Typically, it is used for a weight saving of polyvinyl chloride products. Molding equipment is shown in drawing 2. The metallic mold 22 which has the radiation irradiation window 22a is attached to the twin screw extruder 21, and it is further equipped with the cooling mold 23, the cooling water pool 24, and the taking over machine 25.

[0038]It supplies, a resin compound (a pellet or a grinding article which kneaded resin, a

bulking agent, etc. beforehand) made to foam in the hopper 26 of the twin screw extruder 21, and a foaming agent, for example, a calcium hydride, and melt kneading of resin and the foaming agent is carried out in the first half of the twin screw extruder 21. Next, considering it as predetermined shape with the metallic mold 22, and irradiating with an electron beam from the radiation irradiation window 22a, carrying out extrusion foaming of the resin from the metallic mold 22, cooling with the cooling mold 23 promptly, and making a skin on the surface, it foams inside and SERUKA foam is fabricated.

[0039]\*\* the ejection foaming method -- although the ICI method, the UCC method, etc. are in a typical method, if a window of source container is attached to a resin rich area ball at the tip of a barrel, by this invention, any method is applicable. An outline is explained with reference to drawing 3. The mechanical gate 34 is provided and the injection molding machine 31 which has the radiation irradiation window 33a is used for a tip part of the barrel 33 which the screw 32 backed. For example, when making polypropylene foam, beforehand, melt kneading of polypropylene and a foaming agent, for example, the 4-nitrobenzene diazonium hexafluorophosphate, is carried out, and it is pelletized. Foaming of the resin kneaded material is ejected and carried out into the metallic mold 36, introducing this pellet from the hopper 35, carrying out melt kneading with the screw 32, measuring a predetermined quantity (state which a screw backed), and irradiating with \*\*\*\* of a high-pressure mercury-vapor lamp from the radiation irradiation window 33a. Various foaming methods of the above-mentioned \*\* - \*\* are illustration to the last, and foaming methods other than the above may be used for them by a manufacturing method of an invention of claim 1.

[0040]It is not limited in particular for a concrete process of a manufacturing method of an invention of a statement as well as a case of the invention according to claim 1 to concrete process claim 2 of a manufacturing method of the invention according to claim 2. That is, a general method for manufacturing a resin-molding article which contains air bubbles for usual foam or a weight saving can be used suitably. As a typical manufacturing method, the following \*\* extrusion-foaming methods, the \*\* ordinary pressure foaming method, the \*\* bead foaming method, the \*\* chemical reaction foaming method, the \*\* SERUKA foaming method, the \*\* press foaming method, the \*\* ejection foaming method, etc. can be mentioned.

[0041]\*\* Use an extrusion-foaming device shown in extrusion-foaming method drawing 4. An extrusion-foaming device attaches the metallic mold 42 which has the radiation irradiation window 42a, from a tip of the metallic mold 42, extrudes a foaming agent to the 1 axis extrusion machine 41, and fabricates it directly to it. In the extrusion machine 41, the inlet 43 for pouring in a foaming agent in the middle of a barrel is formed, and the foaming agent potting machine 44 is attached to the inlet 43.

[0042]Supply resin and a foam formation generating agent which are made to foam in the hopper 45 of the 1 axis extrusion machine 41, for example, 4-bromobenzene diazonium



tetrafluoroborate, carry out melt kneading of resin and the foam formation generating agent, and in the first half of the 1 axis extrusion machine 41 as a foaming agent from the middle, For example, press fit carbon dioxide which is a physics type foaming agent, and it is made to dissolve in resin, and adjusts to a temperature suitable for foaming with the metallic mold 42. It lets the radiation irradiation window 42a pass by a tip part of the metallic mold 42, and irradiates with light from a high-pressure mercury-vapor lamp (80W), and extrusion foaming of the resin is carried out from the metallic mold 42 after an appropriate time. Here, although it can adjust by a dose of radiation, and a kind of light source and pass time of resin, a light source is usually selected so that it may end by irradiation time for about several seconds.

[0043]\*\* It is the method which mixed the ordinary pressure foaming method heat decomposition type blowing agent to resin, and was fabricated in predetermined shape and to which carry out afterbaking, and decompose into and a heat decomposition type blowing agent is made to foam. An outline of a device used for the ordinary pressure foaming method is shown in drawing 5. It has the structure of attaching the metallic mold 52 which has the radiation irradiation window 52a in the usual twin screw extruder 51. Predetermined shape, for example, a sheet, is fabricated and foam is fabricated by crosslinking process and a foaming process after an appropriate time.

[0044]For example, when fabricating electron beam cross-linked polyethylene foam, polyethylene, acetic acid 4-methyl phenol as a foam formation generating agent, and AZOJI carvone amide are supplied from the hopper 53, melt kneading is carried out with the twin screw extruder 51, and it is considered as predetermined shape (sheet shaped) within the metallic mold 52. Next, before kneaded material comes out of the metallic mold 52, it irradiates with light of a metal halide lamp (120W) from the radiation irradiation window 52a, and extrusion molding is completed. After an appropriate time, it irradiates with an electron beam with an electron beam acceleration machine, and a bridge is constructed, heat foaming of the polyethylene is further carried out with an ordinary pressure foaming machine, and foam is fabricated. In this case, when the radiation irradiation window 52a is not formed in the metallic mold 52, foam formation generating and bridge construction may be simultaneously performed at the time of electron beam bridge construction. In this case, generating of gas from a foam formation generating agent and bridge construction of resin can be simultaneously performed by carrying out resin temperature of a sheet near the melting point of polyethylene (low density polyethylene 100 \*\*), and performing electron beam irradiation.

[0045]\*\* The bead foaming method this gentleman method is used abundantly obtaining foam of polystyrene. In the twin screw extruder 51 as shown in drawing 5, melt kneading of polystyrene, and a foam formation generating agent, for example, dibutyl ketone, is carried out, and it irradiates with radiation through the radiation irradiation window 52a in a tip end part of the metallic mold 52, and fabricates in bead shape after an appropriate time. An obtained

bead, and a foaming agent and suspension dispersant are heated by an impregnating tub, it impregnates and dries [ wash, dry and ], and a bead is obtained. In this case, it may coat in order to aim at prevention from blocking in a bead.

[0046]Next, heat foaming is carried out with a steam by making an obtained bead into a pre-expansion process, and predetermined foamed beads are manufactured. In the aging process, gas in foam formation is replaced by air, a bead is introduced in a predetermined mold, heat foaming is further carried out with a steam, and mold goods are manufactured.

[0047]\*\* It is the method used as a typical process of foam of the chemical reaction foaming method thermosetting urethane resin. A foam formation generating agent, for example, a magnesium hydride, and a catalyst, polyol, and a foaming agent, for example, pentane, are mixed beforehand, Next, it mixes with polyisocyanate and introduces on a predetermined mold and a belt, before a polymerization reaction occurs, it irradiates with an electron beam, and gasification of a reaction and a foaming agent is caused after an appropriate time, and foam is fabricated.

[0048]\*\* The SERUKA foaming method this gentleman method is a method used as a weight saving method of rigid resin represented by polyvinyl chloride, and is performed using molding equipment of drawing 2 mentioned above.

[0049]In the hopper 26 of the twin screw extruder 21, a resin compound (a pellet or a grinding article which kneaded resin, a foaming agent, a bulking agent, etc. beforehand), Supply a foam formation generating agent, for example, a calcium hydride, and melt kneading of resin and the foam formation generating agent is carried out in the first half of the extrusion machine 21, Considering it as predetermined shape with the metallic mold 22, irradiating with an electron beam from the radiation irradiation window 22a, carrying out extrusion foaming of the resin from the metallic mold 22 after an appropriate time, quenching with the cooling mold 23, and forming a skin in the surface, it foams inside and SERUKA foam is fabricated.

[0050]\*\* A press foaming Homoto method is an extrusion machine, beforehand, carries out melt kneading of the cross linking agent resin, a heat decomposition type blowing agent, a foam formation generating agent, and if needed, and fabricates it in predetermined shape within a metallic mold. In this case, it irradiates with radiation and a foam formation generating agent is made to decompose and gasify. After an appropriate time, a Plastic solid acquired in a press die is introduced, by carrying out application-of-pressure heating, a heat decomposition type blowing agent (decomposing a cross linking agent, when a cross linking agent exists further) is made to disassemble and gasify, and foam is fabricated.

[0051]\*\* the ejection foaming method -- although the ICI method, the UCC method, etc. are in a typical method, as long as an irradiated radiation window of source container can be attached to a resin rich area ball at the tip of a barrel, by the invention according to claim 2, any method is applicable. It can carry out using a device shown in drawing 3.

[0052]For example, in making polypropylene foam. A thing which carried out melt kneading of polypropylene and a foam formation generating agent, for example, the 4-nitrobenzene diazonium hexafluorophosphate, and made it pelletize beforehand, As a foaming agent, AZOJI carvone amide is introduced from the hopper 35, melt kneading is carried out with the screw 32, for example, a predetermined quantity is irradiated with light of a high-pressure mercury-vapor lamp from measuring (state which a screw backed), and the radiation irradiation window 33a, and foaming of the resin kneaded material is ejected and carried out immediately after and into the metallic mold 36.

[0053]Also in a manufacturing method of the invention according to claim 2, foaming methods other than the above-mentioned foaming method may be used like a case of the invention according to claim 1.

[0054]

[Function]In the manufacturing method of the foam of an invention of claim 1, it decomposes by irradiating radiation as mentioned above as a foaming agent, and the foaming agent which generates gas is used. Therefore, only by irradiating with radiation the mixture obtained by mixing the above-mentioned foaming agent to resin, the above-mentioned foaming agent will decompose, gas will be generated, and air bubbles will be formed.

[0055]Therefore, foam can be manufactured with easy equipment. And when the foaming agent which can irradiate with the above-mentioned radiation, decomposes and generates gas is used so that clearly from the below-mentioned example, compared with the case where the conventional heat decomposition type blowing agent is used, the air bubbles of a small path can be formed certainly.

[0056]In the manufacturing method of the foam of an invention of claim 2, radiation decomposes into the resin in which the foaming agent is distributed beforehand, and the above-mentioned foam formation generating agent which generates gas is mixed. Therefore, only by irradiating the obtained resin mixture with radiation, the above-mentioned foam formation generating agent decomposes, gas is generated, and air bubbles are generated. Therefore, when carrying out foaming using the foaming agent which is mixed in addition to the foam formation generating agent, Since the path of the first air bubbles that the air bubbles formed of the foam formation generating agent can grow promptly, and can obtain the foam of desired expansion ratio easily, and are formed of the above-mentioned foam formation generating agent can be controlled with high precision and easily, Compared with the case where only the conventional heat decomposition type blowing agent is used, the air bubbles of a small path can be formed certainly.

[0057]

[Example]Hereafter, this invention is clarified by describing an un-restrictive example. The following Examples 1-8 are examples concerning the invention according to claim 1.

Examples 9-22 are examples concerning the invention according to claim 2.

[0058]It carried out using the extrusion-foaming equipment shown in example 1 drawing 1. ABS-plastics (Toray Industries [, Inc. ] make trade name: TOYORAKKU 400, rate of bending flexibility  $26,000 \text{ kg/cm}^2$ ) 100 weight section, and 4-bromobenzene diazonium tetrafluoroborate 2.0 weight section, Using the twin screw extruder (the diameter of 30 mm, ratio-of-length-to-diameter=30) 11, at 160 \*\*, carry out melt kneading and by the tip part of the metallic mold 12. It irradiated with the light of the high-pressure mercury-vapor lamp (80W) through the radiation irradiation window 12a which consists of sapphire glass, the foaming agent was disassembled and gasified, it extruded from the metallic mold (temperature is 155 \*\*) 12 to horseshoe-shaped 1 second afterward, and foam was fabricated. The expansion ratio of the obtained foam was 2.9, the average cell diameter was 4.0 micrometers and the rate of bending flexibility was  $20,000 \text{ kg/cm}^2$ .

[0059]It carried out using the extrusion-foaming device shown in example 2 drawing 1. polystyrene (Asahi Chemical [ Co., Ltd. ] make trade name: Styron 666R, rate of bending flexibility  $36,000 \text{ kg/cm}^2$ ) 100 weight section, and magnesium hydride 1.2 weight section -- a twin screw extruder (the diameter of 30 mm.) Using ratio-of-length-to-diameter=30 11, at 180 \*\*, carry out melt kneading and by the tip part of the metallic mold 12. It irradiated with the electron beam so that an absorbed dose might be set to 2MRad with an electron-beam-irradiation machine (300 kV) through the radiation irradiation window 12a which consists of sapphire glass, and the foaming agent was disassembled and gasified, it extruded from the metallic mold (temperature of 160 \*\*) 12 to the sheet shaped 0.5 second afterward, and foam was fabricated. As for the expansion ratio of foam, 3.9 micrometers and the rate of bending flexibility of 2.2 times and an average cell diameter were  $32,000 \text{ kg/cm}^2$ .

[0060]Using example 3 twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30), melt kneading of polystyrene (the Asahi Chemical [ Co., Ltd. ] make, a trade name: Styron 475S) and the dibutyl ketone 7.5 weight section was carried out at 180 \*\*, and it fabricated in bead shape.

[0061]Heating the obtained bead with a 160 \*\* steam, irradiated with the electron beam so that an absorbed dose might serve as 2MRad with an electron-beam-irradiation machine (300 kV), and decompose and gasify a foaming agent, it was made to foam, and foamed beads were manufactured. Next, foamed beads were dried and ventilation aging of 24 hours was performed. These foamed beads were introduced in the metallic mold, heat foaming was carried out with a 130 \*\* steam, and foam was fabricated. As for 18 times and an average cell diameter, the thermal conductivity of 3.3 micrometers and the rate of a closed cell was [ expansion ratio of the obtained foam ]  $0.022 \text{ Kcal/m-hand}^{**} 93\%$ .

[0062]Using example 4 twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30), melt kneading of polypropylene (Himont make and trade name:HMS PF814) and the 4-chlorobenzene diazonium hexafluorophosphate 5.0 weight section was carried out at 190 \*\*, and it fabricated in bead shape.

[0063]The obtained bead was heated with a 190 \*\* steam, it irradiated with the light of the high-pressure mercury-vapor lamp (120W), the foaming agent was disassembled and gasified, and foamed beads were manufactured. Next, foamed beads were dried and ventilation aging of 48 hours was performed. These foamed beads were introduced in the metallic mold, heat foaming was carried out with a 170 \*\* steam, and foam was manufactured. As for 10 times and an average cell diameter, the thermal conductivity of 2.5 micrometers and the rate of a closed cell was [ expansion ratio of foam ] 0.025Kcal/m-hand\*\* 94%.

[0064]Example 5 aromatic-amine system polyol (Sumitomo Beyer urethane company make and trade name:H422, OH radical value 412) 100 weight section, Dibutyltin dilaurate 0.5 weight section, polyol denaturation silicone (Toray Industries Dow Corning make and trade name:SH193) 2.5 weight section, and 4-bromobenzene diazonium tetrafluoroborate 7.0 weight section were mixed, drying desiccation was carried out, and mixed liquor was obtained. next, the denaturation MDI (the Sumitomo Beyer urethane company make.) which carried out drying desiccation at this mixed liquor Trade name: 44V20, and 31.5 % of the weight of NCO content 59 weight sections are mixed with an agitator (it is supposed that the above-mentioned OH radical value and a NCO content are equivalent), a 100mmx100mmx2mm concave is filled with liquid, it irradiated with the light of the high-pressure mercury-vapor lamp (120W), and it was made to foam immediately. As for 21 times and an average cell diameter, the thermal conductivity of 5.4 micrometers and the rate of a closed cell was [ expansion ratio of foam ] 0.022Kcal/m-hand\*\* 89%.

[0065]It carried out using the extrusion-foaming device shown in example 6 drawing 2. ABS-plastics 100 weight section used in Example 1, and magnesium hydride 2.0 weight section, It kneads at 180 \*\* using the twin screw extruder (the diameter of 50 mm, ratio-of-length-to-diameter=35) 21, With the metallic mold 22 which has the radiation irradiation window 22a which consists of sapphire glass all over width at the tip of the metallic mold 22, from this radiation irradiation window 22a. It irradiated with the electron beam so that an absorbed dose might be set to 12MRad with an electron-beam-irradiation machine (1000 kV), and the foaming agent was disassembled and gasified, and it extruded from the metallic mold (temperature of 175 \*\*) 22 to horseshoe-shaped 0.2 second afterward, and introduced into the cooling mold 23, and foam was fabricated. As for the expansion ratio of foam, 0.5 micrometer and the rate of bending flexibility of 1.9 times and an average cell diameter were 38,000 kg/cm<sup>2</sup>.

[0066]It produced with the device shown in example 7 drawing 3. Polyamide (Showa Denko [ K.K. ] make trade name: Taegu Neele A216, rate of bending flexibility 29,000 kg/cm<sup>2</sup>) 100 dry

enough weight section, Melt kneading of the 4-nitrobenzene diazonium hexafluorophosphate 1.2 weight section was carried out, and it was made to pelletize at 250 °C using a twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30). Next, the above-mentioned pellet is supplied to the hopper 35 of the 75-t injection molding machine 31, Melt kneading was carried out at 240 °C, a predetermined quantity was measured (state which the screw 32 backed), it irradiated with the light of the high-pressure mercury-vapor lamp (120W) from the radiation irradiation window 33a, and the foaming agent was disassembled and gasified, 0.5 second afterward, it ejected in the metallic mold (100mmx80mmx5m sheet shaped) 36, and foam was fabricated. As for the expansion ratio of the obtained foam, 0.7 micrometer and the rate of bending flexibility of 1.6 times and an average cell diameter were 28,000 kg/cm<sup>2</sup>.

[0067]It produced with the device shown in example 8 drawing 3. Polyacetal (Du Pont make trade name: Dirlin 500, rate of bending flexibility 29,000 kg/cm<sup>2</sup>) 100 dry enough weight section, Melt kneading of the Diazo RED RC0.2 weight section was carried out, and it was made to pelletize at 260 °C using a twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30). Next, a pellet is supplied to the hopper 35 of the 75-t injection molding machine 31, Melt kneading was carried out at 240 °C, a predetermined quantity was measured (state which the screw 32 backed), it irradiated with the light of the high-pressure mercury-vapor lamp (120W) from the radiation irradiation window 33a, and the foaming agent was disassembled and gasified, 0.2 second afterward, it ejected in the metallic mold (100mmx80mmx5m sheet shaped), and foam was fabricated. As for the expansion ratio of the obtained foam, 0.4 micrometer and the rate of bending flexibility of 1.3 times and an average cell diameter were 29,000 kg/cm<sup>2</sup>.

[0068]It carried out using the extrusion-foaming device shown in comparative example 1 drawing 1. ABS-plastics 100 weight section used in Example 1, and AZOJI carvone amide (the Otsuka Chemical Co., Ltd. make.) Trade name: Using the twin screw extruder (the diameter of 30 mm, ratio-of-length-to-diameter=30) 11, melt kneading of the uniform AZH1.8 weight section was carried out at 180 °C, it was extruded from the metallic mold (temperature of 155 °C) 12 to horseshoe-shaped, and foam was fabricated. As for the expansion ratio of foam, 150 micrometers and the rate of bending flexibility of 2.6 times and an average cell diameter were 10,000 kg/cm<sup>2</sup>.

[0069]Melt kneading of the polystyrene (Asahi Chemical [ Co., Ltd. ] make trade name: Styron 475S) and AZOJI carvone amide (Otsuka Chemical [ Co., Ltd. ] make trade name: uniform AZHNM) 10 weight section was carried out at 160 °C with the comparative example 2 twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30) 11, and it fabricated in bead shape.

[0070]Next, this bead was heated with a 180 °C steam, and desiccation and ventilation aging of

24 hours were performed for foamed beads manufacture and after that. These foamed beads were introduced in the metallic mold, heat foaming was carried out with a 130 °C steam, and mold goods were manufactured. As for 17 times and an average cell diameter, the thermal conductivity of 120 micrometers and the rate of a closed cell was [ expansion ratio of foam ] 0.030Kcal/m-hand\*\* 93%.

[0071]Comparative example 3 aromatic-amine system polyol (Sumitomo Beyer urethane company make and trade name:H422, OH radical value 412) 100 weight section, With dibutyltin dilaurate 0.5 weight section and polyol denaturation silicone (Toray Industries Dow Corning make and trade name:SH193) 2.5 weight section, 16 weight sections were mixed, drying desiccation of the HCFC142b was carried out, and mixed liquor was obtained. next, the denaturation MDI (the Sumitomo Beyer urethane company make.) which carried out drying desiccation at this mixed liquor Trade name: 44V20, and 31.5 % of the weight of NCO content 59 weight sections were added (as a result, OH radical value and a NCO content, equivalent weight), it mixed with the agitator, and liquid was made to pour and foam to a 100mmx100mmx2mm concave. Then, for three weeks, it was neglected under ordinary temperature and foam was obtained. As for 22 times and an average cell diameter, the thermal conductivity of 100 micrometers and the rate of a closed cell was [ expansion ratio of foam ] 0.029Kcal/m-hand\*\* 92%.

[0072]It carried out using the extrusion-foaming device shown in comparative example 4 drawing 2. ABS-plastics 100 weight section and sodium bicarbonate 1.0 weight section which were used in Example 1 were kneaded at 180 °C using the twin screw extruder (the diameter of 50 mm, ratio-of-length-to-diameter=35) 21, and it extruded from the metallic mold (temperature of 175 °C) 22 to horseshoe-shaped, and introduced into the cooling mold 23, and foam was fabricated. As for the expansion ratio of foam, 80 micrometers and the rate of bending flexibility of 1.6 times and an average cell diameter were 28,000 kg/cm<sup>2</sup>.

[0073]It produced with the device shown in comparative example 5 drawing 3. Polyamide (Showa Denko [ K.K. ] make trade name: Taegu Neele A216, rate of bending flexibility 29,000 kg/cm<sup>2</sup>) 100 dry enough weight section, Melt kneading of the AZOJI carvone amide 1.2 weight section used by the comparative example 2 was carried out, and it was made to pelletize at 250 °C using a twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30). Next, the pellet was supplied to the hopper 35 of the 75-t injection molding machine 31, melt kneading was carried out at 240 °C, a predetermined quantity was measured (state which the screw 32 backed), it ejected in the metallic mold (sheet shaped which is 100mmx80mmx5mm) 36, and foam was fabricated. As for the expansion ratio of the obtained foam, 90 micrometers and the rate of bending flexibility of 1.5 times and an average cell diameter were 21,000 kg/cm<sup>2</sup>.

[0074]The extrusion-foaming device shown in example 9 drawing 4 was used. Low-density-polyethylene (TOSOH [ CORP. ] make trade name: PETORSEN 340) 100 weight section and 4-bromobenzene diazonium tetrafluoroborate 0.1 weight section were beforehand kneaded and pelletized at 140 °C using the twin screw extruder (the diameter of 30 mm, ratio-of-length-to-diameter=30). the 1 axis extrusion machine (the diameter of 65 mm.) which shows drawing 4 the pellet obtained as mentioned above Introduce into the hopper 45 of ratio-of-length-to-diameter=36 41 and carbon dioxide is pressed fit by the pressure of 50 kg/cm<sup>2</sup> from the middle, It was made to dissolve in resin, and irradiated with the light of the high-pressure mercury-vapor lamp through the radiation irradiation window 42a which consists of sapphire glass in the tip part of the metallic mold 42, the foam formation generating agent was decomposed and gasified, the temperature of the metallic mold 42 was 110 °C 2 seconds afterward, and extrusion and a foaming object were acquired from the metallic mold 42 to tube shape. The average cell diameter was 2.0 micrometers, the expansion ratio of the obtained foam was 12 and the rate of a closed cell was [ thermal conductivity ] 0.024Kcal/m-hand\*\* 95%.

[0075]The extrusion-foaming device shown in example 10 drawing 4 was used. Polystyrene (Asahi Chemical [ Co., Ltd. ] make trade name: Styron 666R) 100 weight section and magnesium hydride 0.5 weight section were beforehand kneaded and pelletized at the temperature of 180 °C using the twin screw extruder (the diameter of 30 mm, ratio-of-length-to-diameter=30). the 1 axis extrusion machine (the diameter of 65 mm.) which shows drawing 4 the pellet obtained as mentioned above Introduce into the hopper 45 of ratio-of-length-to-diameter=36 41, press fit so that HCFC141b may be set to 10 g from the middle to 100 g of polystyrene, make it dissolve in resin, and by the tip part of the metallic mold 42. It glared so that an absorbed dose might be set to 2MRad with an electron-beam-irradiation machine (300 kV) through the radiation irradiation window 42a which consists of sapphire glass, the foam formation generating agent was decomposed and gasified, and the temperature of the metallic mold 42 was 160 °C 0.5 second afterward, it extruded from the metallic mold 42 to the sheet shaped, and the foaming object was fabricated. As for 18 times and an average cell diameter, the thermal conductivity of 1.2 micrometers and the rate of a closed cell was [ expansion ratio of the obtained foam ] 0.022Kcal/m-hand\*\* 88%.

[0076]The general-purpose equipment for launching shown in example 11 drawing 5 was used. Compound (central chemicals company make and trade name:SE5) 100 weight section for inorganic bulking agent content VCM/PVC foaming, Barium hydride 1.0 weight section is kneaded with the twin screw extruder (the diameter of 60 mm, ratio-of-length-to-diameter=35) 51, It irradiated with the electron beam so that an absorbed dose might be set to 10MRad from an electron-beam-irradiation machine (1000 kV) through the radiation irradiation window 52a in the tip part of the metallic mold 52, and the foam formation generating agent was decomposed



and gasified. The temperature of the metallic mold 52 was 175 °C 0.2 second after the exposure of the above-mentioned electron beam, it extruded from the metallic mold 52 to the sheet shaped, and the foaming object was acquired. As for 3.5 times and an average cell diameter, the rate of bending flexibility of 8.5 micrometers and the rate of a closed cell was

[ expansion ratio of the obtained foam ] 35,000 kg/cm<sup>2</sup> 100%.

[0077]The device shown in example 12 drawing 5 was used. Low-density-polyethylene (Sumitomo Chemical [ Co., Ltd. ] make trade name: SUMIKASEN G401) 100 weight section, AZOJI carvone amide (Otsuka Chemical [ Co., Ltd. ] make [ the following, ADCA, ] trade name: uniform AZH) 15 weight section, 4-nitrobenzene diazonium hexafluorophosphate 0.2 weight section -- a twin screw extruder (the diameter of 50 mm.) Using ratio-of-length-to-diameter=35 51 from this radiation irradiation window 52a of T mold sheet metallic mold which kneads at 140 °C and has the radiation irradiation window 52a in the tip part of the metallic mold 52 all over sheet width. It irradiated with the high-pressure mercury-vapor lamp (120W), the foam formation generating agent was decomposed and gasified, the die temperature was 130 °C 1.5 seconds afterward, and the sheet (300 mm in width and 1 mm in thickness) was extruded and fabricated from the metallic mold 52. Next, it irradiated with the electron beam so that an exposure dose might become the fabricated sheet with 6MRad, and it foamed in 200 °C oven. [0078]the obtained foam -- 30 times and an average cell diameter were 4.9 micrometers, and the rate of a closed cell was [ width / 870 mm and thickness / the thermal conductivity of 2.8 mm and expansion ratio ] 0.023Kcal/m-hand °C 97%.

[0079]The device shown in example 13 drawing 5 was used. Low-density-polyethylene (company make [ Mitsui petrochemical ] trade name: Myra Son B324) 80 weight section, Ultra-low-density-polyethylene (Sumitomo Chemical [ Co., Ltd. ] make trade name: excellent VL200) 20 weight section, AZOJI carvone amide (Otsuka Chemical [ Co., Ltd. ] make [ the following, ADCA, ] trade name: uniform AZH) 13 weight section, 4-nitrobenzene diazonium hexafluorophosphate 0.3 weight section -- a twin screw extruder (the diameter of 50 mm.) Using ratio-of-length-to-diameter=35 51 from this radiation irradiation window 52a of T mold sheet metallic mold which kneads at 140 °C and has the radiation irradiation window 52a in metallic mold 52 tip part all over sheet width. It irradiated with the light of the high-pressure mercury-vapor lamp (120W), the foam formation generating agent was decomposed and gasified, the die temperature was 130 °C 1.5 seconds afterward, and the sheet (300 mm in width and 1 mm in thickness) was extruded and fabricated from the metallic mold 52. Next, it irradiated with the electron beam so that an exposure dose might become the fabricated sheet with 5MRad, and it foamed in 200 °C oven.

[0080]the obtained foam -- 25 times and an average cell diameter were 2.1 micrometers, and the rate of a closed cell was [ width / 850 mm and thickness / the thermal conductivity of 2.5 mm and expansion ratio ] 0.023Kcal/m-hand °C 93%.

[0081]the twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30) 51 shown in example 14 drawing 5 -- polystyrene (the Asahi Chemical Co., Ltd. make.) Trade name : Carry out 180 \*\* melt kneading of Styron 475S100 weight section and the dibutyl ketone 0.2 weight section, and it lets the radiation irradiation window 52a pass at the metallic mold tip, It irradiated with the light of the high-pressure mercury-vapor lamp (120W), the foam formation generating agent was decomposed and gasified, the die temperature was 170 \*\* 1.5 seconds afterward, and it extruded in the shape of a bead. Water 200 weight section which distributed polyvinyl alcohol 0.5 weight section was made to distribute bead 100 obtained weight section and pentane 5 weight section, and temperature was 80 \*\* and was neglected for 2 hours. Next, heat foaming of the above-mentioned bead was carried out with a 160 \*\* steam, foamed beads were manufactured, it dried after an appropriate time, and ventilation aging of 24 hours was performed. Ripe foamed beads were introduced in the metallic mold, heat foaming was carried out with a 130 \*\* steam, and mold goods were obtained.

[0082]The expansion ratio of the obtained foam was 15, the average cell diameter was 1.1 micrometers, the rate of a closed cell was 96%, and thermal conductivity was 0.021Kcal/m-hand\*\*.

[0083]the twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30) 51 shown in example 15 drawing 5 -- polypropylene (the Himont make.) Trade name : Carry out melt kneading of HMS PF814 100 weight section and the 4-chlorobenzene diazonium hexafluorophosphate 0.2 weight section at 190 \*\*, and it lets the radiation irradiation window 52a pass at the tip of the metallic mold 52, It irradiated with the light of the high-pressure mercury-vapor lamp (120W), the foam formation generating agent was decomposed and gasified, the die temperature was 180 \*\* 2.0 seconds afterward, and it extruded in the shape of a bead. Bead 100 obtained weight section and water 200 weight section which distributed polyvinyl alcohol 0.5 weight section for seven weight sections were made to distribute HCFC142b, and temperature was 130 \*\* and was neglected for 2 hours. Next, heat foaming of the above-mentioned bead was carried out with a 190 \*\* steam, foamed beads were manufactured, it dried after an appropriate time, and ventilation aging of 48 hours was performed. Ripe foamed beads were introduced in the metallic mold, heat foaming was carried out with a 170 \*\* steam, and mold goods were obtained.

[0084]The expansion ratio of the obtained foam was 13, the average cell diameter was 0.8 micrometer, the rate of a closed cell was 98%, and thermal conductivity was 0.024Kcal/m-hand\*\*.

[0085]Example 16 aromatic-amine system polyol (Sumitomo Beyer urethane company make and trade name:H422, OH radical value 412) 100 weight section, HCFC142b 22 weight sections and dibutyltin dilaurate 0.5 weight section, Polyol denaturation silicone (Toray Industries Dow Corning make and trade name:SH193) 2.5 weight section and 4-

bromobenzene diazonium tetrafluoroborate 0.3 weight section were mixed, drying desiccation was carried out, and mixed liquor was prepared. next, the denaturation MDI (the Sumitomo Beyer urethane company make.) which carried out drying desiccation at this mixed liquor Trade name: Added 44V20, and 31.5 % of the weight of NCO content 59 weight sections (OH radical value and NCO content are equivalent weight), mixed with the agitator, and filled the 100mmx100mmx2mm mold with mixed liquor, and irradiate with the light of a high-pressure mercury-vapor lamp (120W), it was made to foam promptly, and foam was obtained. The expansion ratio of the obtained foam was 30, the average cell diameter was 7.9 micrometers, the rate of a closed cell was 86%, and thermal conductivity was 0.015Kcal/m-hand\*\*.

[0086]It produced using the molding equipment shown in example 17 drawing 2. Compound (Nippon Zeon Co., Ltd. make and trade name:C1) 100 weight section for VCM/PVC SERUKA foaming, magnesium hydride 1.0 weight section -- a twin screw extruder (the diameter of 50 mm.) Using ratio-of-length-to-diameter=35 21, with the metallic mold 22 which kneads at 180 \*\* and has the radiation irradiation window 22a which consists of sapphire glass all over width at the tip of a metallic mold from this radiation irradiation window 22a. It glared so that an absorbed dose might be set to 12MRad with an electron-beam-irradiation machine (1000 kV), and the foam formation generating agent was decomposed and gasified, extrusion foaming was carried out to horseshoe-shaped as a die temperature of 175 \*\* 0.2 second afterward, it introduced into the cooling mold 23, and the foaming article was produced. The expansion ratio of foam was 1.6, the average cell diameter was 0.5 micrometer, and the rate of bending flexibility was 38,000 kg/cm<sup>2</sup>.

[0087]the twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30) 51 as shown in example 18 drawing 5 -- high density polyethylene (the TOSOH CORP. make.) trade name: -- NIPORON hard 6000 100 weight section and dibutyl peroxide (the Nippon Oil & Fats Co., Ltd. make.) Trade name : Half-life temperature 1.0 weight section during par butyl D; 1 minute of 185.9 \*\*, ADCA(Otsuka Chemical [ Co., Ltd. ] make trade name: uniform AZHM)15 weight section, Carry out melt kneading of the 4-chlorobenzene diazonium hexafluorophosphate dibutyl ketone 0.2 weight section at 145 \*\*, and it lets the radiation irradiation window 52a pass by the tip part of the metallic mold 52, It irradiated with the light of the high-pressure mercury-vapor lamp (120W), the foam formation generating agent was decomposed and gasified, and it extruded to the sheet shaped with the die temperature of 135 \*\* 0.2 second afterward. Next, this sheet was fed into a 180 \*\* press, and it was made to foam in one step. The average cell diameter was 3.7 micrometers, the expansion ratio of the obtained foam was 31 and the rate of a closed cell was [ thermal conductivity ] 0.024Kcal/m-hand\*\* 96%.

[0088]It produced with the equipment shown in example 19 drawing 3. Polyamide (Showa Denko [ K.K. ] make trade name: Taegu Neele A216, rate of bending flexibility 29,000 kg/cm<sup>2</sup>)

100 dry enough weight section, Melt kneading of the 4-nitrobenzene diazonium hexafluorophosphate 0.3 weight section was carried out, and it was made to pelletize at 250 °C using a twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30). Next, the pellet and ADCA2.0 weight section which carried out the dry blend to the hopper 35 of the 75-t injection molding machine 31 are supplied, Carry out melt kneading at 240 °C, and a predetermined quantity is measured (state which the screw 32 backed), It irradiated with the light of the high-pressure mercury-vapor lamp (120W) from the radiation irradiation window 33a, and the foam formation generating agent was decomposed and gasified, 0.5 second afterward, it ejected in the metallic mold (100mmx80mmx5m sheet shaped) 36, and foam was fabricated. As for the expansion ratio of the obtained foam, 2.2 micrometers and the rate of bending flexibility of 3.6 times and an average cell diameter were 26,000 kg/cm<sup>2</sup>.

[0089]It produced with the equipment (what has an insufflation hole in the middle of a barrel) roughly shown in [example 20 drawing 3](#). Polyacetal (Du Pont make trade name: Dirlin 500, rate of bending flexibility 29,000 kg/cm<sup>2</sup>) 100 dry enough weight section, Melt kneading of the Diazo RED RC0.2 weight section was carried out, and it was made to pelletize at 260 °C using a twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30). Next, the pellet which carried out the dry blend to the hopper 35 of the 200-t injection molding machine which has insufflation equipment in the middle of a barrel is supplied, Carry out melt kneading at 240 °C, and carbon dioxide is pressed fit in continuation by 20 kg/cm<sup>2</sup> from the barrel middle, A predetermined quantity was measured (state which the screw 32 backed), it irradiated with the light of the high-pressure mercury-vapor lamp (120W) from the radiation irradiation window 33a, and the foam formation generating agent was decomposed and gasified, 0.2 second afterward, it ejected in the metallic mold (100mmx80mmx5m sheet shaped) 36, and foam was fabricated. As for 6.4 times and an average cell diameter, 17,000 kg/cm<sup>2</sup> and the thermal conductivity of 0.7 micrometer and the rate of bending flexibility were [ expansion ratio of the obtained foam ] 0.032Kcal/m-hand°C.

[0090]the twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30) 51 as shown in [example 21 drawing 5](#) -- ABS (the Toray Industries, Inc. make.) Trade name : Carry out melt kneading of TOYORAKKU 400, rate <sup>2</sup>[ of 26,000kg/cm ] of bending flexibility 100 weight section and dibutyl ketone 1.0 weight section, and the hydrocarbon sodium 1 weight section at 180 °C, and it lets the exit window 52a pass at the tip of the metallic mold 52, It irradiated with the high-pressure mercury-vapor lamp (120W) from four directions, the foam formation generating agent was decomposed and gasified, and extrusion foaming was carried out to hollow deck shape 0.1 second afterward. As for the expansion ratio of the obtained foam, 1.4 micrometers and the rate of bending flexibility of 1.7 times and an average cell diameter were 26,000 kg/cm<sup>2</sup>.

[0091]the 1 axis extrusion machine (the diameter of 30 mm.) which has the injected hole 43 in the middle of a barrel as shown in example 22 drawing 4 Melt kneading of ABS(Toray Industries [ , Inc. ] make trade name: TOYORAKKU 400, rate of bending flexibility 26,000 kg/cm<sup>2</sup>) 100 weight section and the 4-bromobenzene diazonium tetrafluoroborate 0.3 weight section is carried out at 180 ° ratio-of-length-to-diameter=37.41, Carbon dioxide 20 kg/cm<sup>2</sup> was pressed fit from the barrel middle, and it let the radiation irradiation window 42a pass at the tip of the metallic mold 42, and irradiated with the light of the high-pressure mercury-vapor lamp (120W) from four directions, the foam formation generating agent was decomposed and gasified, and extrusion foaming was carried out to hollow deck shape 0.1 second afterward. As for the expansion ratio of the obtained foam, 0.8 micrometer and the rate of bending flexibility of 2.8 times and an average cell diameter were 22,000 kg/cm<sup>2</sup>.

[0092]The extrusion-foaming equipment shown in comparative example 6 drawing 4 is used. low density polyethylene (the TOSOH [ CORP. ] make, a trade name: PETOROSEN 340) -- a 1 axis extrusion machine (the diameter of 65 mm.) Introduced into the hopper 45 of ratio-of-length-to-diameter=36.41, pressed carbon dioxide fit by the pressure of 50 kg/cm<sup>2</sup> from the middle, and it was made to dissolve in resin, and extruded to tube shape with the die temperature of 110 °, and the foaming article was produced. As for 12 times and an average cell diameter, the thermal conductivity of 350 micrometers and the rate of a closed cell was [ expansion ratio of the obtained foam ] 0.038Kcal/m-hand\*\* 95%.

[0093]The extrusion-foaming equipment shown in comparative example 7 drawing 4 is used. polystyrene (the Asahi Chemical [ Co., Ltd. ] make, a trade name: Styron 666R) -- a 1 axis extrusion machine (the diameter of 65 mm.) Introduced into the hopper 45 of ratio-of-length-to-diameter=36.41, pressed fit so that HCFC141b might be set to 10 g from the middle to 100 g of polystyrene, and it was made to dissolve in resin, and extruded to the sheet shaped with the die temperature of 160 °, and the foaming article was produced. As for 18 times and an average cell diameter, the thermal conductivity of 250 micrometers and the rate of a closed cell was [ expansion ratio of the obtained foam ] 0.033Kcal/m-hand\*\* 88%.

[0094]The extrusion equipment shown in comparative example 8 drawing 5 is used. The compound for inorganic bulking agent content VCM/PVC foaming (central chemicals company make and trade name:SE5) was kneaded with the twin screw extruder (the diameter of 60 mm, ratio-of-length-to-diameter=35) 51, it extruded to the sheet shaped with the die temperature of 175 °, and the foaming article was obtained. As for 3.3 times and an average cell diameter, the rate of bending flexibility of 150 micrometers and the rate of independent foam formation was [ expansion ratio of the obtained foam ] 26,000 kg/cm<sup>2</sup> 100%.

[0095]The equipment and the process which were shown in comparative example 9 drawing 5 are used. Low-density-polyethylene (Sumitomo Chemical [ Co., Ltd. ] make trade name:

SUMIKASEN G401) 100 weight section, AZOJI carvone amide (Otsuka Chemical [ Co., Ltd. ] make [ the following, ADCA, ] trade name: uniform AZH) 15 weight section was kneaded with the twin screw extruder (the diameter of 50 mm, ratio-of-length-to-diameter=35) 51, and sheet forming was carried out with T mold sheet metallic mold 52. Next, it irradiated with the electron beam so that an exposure dose might become this sheet with 6MRad, and it foamed in 200 \*\* foaming oven.

[0096]the obtained foam – 30 times and an average cell diameter were 230 micrometers, and the rate of a closed cell was [ width / 880 mm and thickness / the thermal conductivity of 2.8 mm and expansion ratio ] 0.028Kcal/m-hand\*\* 98%.

[0097]Melt kneading of the polystyrene (the Asahi Chemical [ Co., Ltd. ] make, a trade name: Styron 475S) was carried out with the twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30) 51 as shown in comparative example 10 drawing 5, and it extruded in the shape of a bead. Water 200 weight section which distributed polyvinyl alcohol 0.5 weight section was made to distribute this bead 100 weight section and pentane 5 weight section, and temperature was prepared at 80 \*\* for 2 hours.

[0098]Next, heat foaming of this bead was carried out with a 160 \*\* steam, foamed beads were manufactured, it dried after an appropriate time, and ventilation aging of 24 hours was performed. These foamed beads were introduced in the metallic mold, heat foaming was carried out with a 130 \*\* steam, and mold goods were obtained. The expansion ratio of the obtained foam was 15, the average cell diameter was 120 micrometers, the rate of a closed cell was 96%, and thermal conductivity was 0.026Kcal/m-hand\*\*.

[0099]Comparative example 11 aromatic-amine system polyol (Sumitomo Beyer urethane company make and trade name:H422, OH radical value 412) 100 weight section and 142bHCFC22 weight section, Dibutyltin laurate 0.5 weight section and polyol denaturation silicone (Toray Industries Dow Corning make and trade name:SH193) 2.5 weight section were mixed, drying desiccation was carried out, and it prepared. Next, denaturation MDI(Sumitomo Beyer urethane company make and trade name:44V20, 31.5 % of the weight of NCO contents) 59 weight section which carried out drying desiccation was added to this mixed liquor (as a result, OH radical value and a NCO content, equivalent weight), it mixed with the agitator, and liquid was made to pour and foam in a 100mmx100mmx2mm mold. As for 30 times and an average cell diameter, the thermal conductivity of 160 micrometers and the rate of a closed cell was [ expansion ratio of foam ] 0.022Kcal/m-hand\*\* 86%.

[0100]It produced using the molding equipment shown in comparative example 12 drawing 2. The compound for VCM/PVC SERUKA foaming (Nippon Zeon Co., Ltd. make and trade name:C1) was kneaded with the twin screw extruder (the diameter of 50 mm, ratio-of-length-to-diameter=35) 21, extrusion foaming was carried out to horseshoe-shaped with the die temperature of 175 \*\*, it introduced into the cooling mold 23, and the foaming article was

produced. The expansion ratio of foam was 1.6, the average cell diameter was 80 micrometers, and the rate of bending flexibility was  $25,000 \text{ kg/cm}^2$ .

[0101]With the twin screw extruder (the diameter of 45 mm, ratio-of-length-to-diameter=30) 51 as shown in comparative example 13 drawing 5, high-density-polyethylene (TOSOH [ CORP. ] make trade name: NIPORON hard 6000) 100 weight section, Melt kneading of par butyl D1.0 weight section used in Example 10 and the ADCA(Otsuka Chemical [ Co., Ltd. ] make trade name: uniform AZHM)15 weight section was carried out, and it extruded to the sheet shaped. Next, this sheet was fed into a 180 °C press, and it was made to foam in one step. The average cell diameter was 100 micrometers, the expansion ratio of the obtained foam was 30 and the rate of a closed cell was [ thermal conductivity ]  $0.028 \text{ Kcal/m-hand}^{\circ\circ}$  98%.

[0102]It produced with the equipment roughly shown in comparative example 14 drawing 3. Polyamide (Showa Denko [ K.K. ] make trade name: Taegu Neele A216, rate of bending flexibility  $29,000 \text{ kg/cm}^2$ ) 100 dry enough weight section, ADCA2.0 weight section used in Example 18 was supplied to the hopper 35 of a 75-t injection molding machine, melt kneading was carried out with the screw 32, it ejected in the metallic mold (100mmx80mmx5m sheet shaped) 36, and foam was fabricated. As for the expansion ratio of the obtained foam, 110 micrometers and the rate of bending flexibility of 3.8 times and an average cell diameter were  $22,000 \text{ kg/cm}^2$ .

[0103]It produced with the equipment (what has an insufflation hole in the middle of a barrel) roughly shown in comparative example 15 drawing 3. The dry enough polyacetal (the Du Pont make, a trade name: Dirlin 500, rate of bending flexibility  $29,000 \text{ kg/cm}^2$ ) is supplied to the hopper 35 of the 200-t injection molding machine which has insufflation equipment in the middle of a barrel, Melt kneading was carried out with the screw 32, from the barrel middle, carbon dioxide was pressed fit in continuation by  $20 \text{ kg/cm}^2$ , a predetermined quantity was measured, it ejected in the metallic mold (100mmx80mmx5m sheet shaped), and foam was fabricated. As for 6.9 times and an average cell diameter,  $11,000 \text{ kg/cm}^2$  and the thermal conductivity of 90 micrometers and the rate of bending flexibility were [ expansion ratio of the obtained foam ]  $0.035 \text{ Kcal/m-hand}^{\circ\circ}$ .

[0104]the twin screw extruder (the diameter of 30 mm.) which has an injected hole in the middle of 16 barrels of comparative examples Melt kneading of ABS (the Toray Industries [ Inc. ] make, a trade name: TOYORAKKU 400, rate of bending flexibility  $26,000 \text{ kg/cm}^2$ ) was carried out by ratio-of-length-to-diameter=37, carbon dioxide  $20 \text{ kg/cm}^2$  was pressed fit from the barrel middle, and extrusion foaming was carried out to hollow deck shape. As for the expansion ratio of the obtained foam, 150 micrometers and the rate of bending flexibility of 2.8 times and an average cell diameter were  $12,000 \text{ kg/cm}^2$ .

[0105]The various measuring methods are as follows.

[Expansion ratio] Apparent density gravity was measured based on JIS K-6767, and the reciprocal was made into expansion ratio.

[0106][Average cell diameter] The freezing fracture of the obtained foam was carried out, the section was photoed with the electron microscope, and the pitch diameter of air bubbles was computed after image processing (circular processing).

[0107][The rate of a closed cell] The rate of a closed cell (%) was measured by 1 - 1 / 2-1-atmosphere method using the air relation hydrometer 1000 type (made by Tokyo Saiensu-Sha).

[0108][Thermal conductivity] Based on JIS A-1412, thermal conductivity (Kcal/m-hand\*\*) was measured.

[0109][Buffer coefficient-C value MIN] It is compression stress ( $\sigma$ ) by the compression measurement by a part for 10-mm/. - It was distorted ( $\epsilon$ ) and asked for the curve, and further, it asked for absorbed energy  $e$  to each value of the compression stress  $\sigma$ , computed by  $C=\sigma/e$ , and was considered as the static stress of the minimum.

[0110][The rate of bending flexibility] The rate of bending flexibility ( $\text{kg}/\text{cm}^2$ ) was measured based on ASTM D790. The result of an example and a comparative example is collectively shown in Table 1 - 9.

[0111]

[Table 1]

	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
発泡倍率 (倍)	2.9	2.2	1.8	1.0	2.1
平均気泡径 ( $\mu\text{m}$ )	4.0	3.9	3.3	2.5	5.4
独立気泡率 (%)	—	—	9.3	9.4	8.9
熱伝導率 Kcal/mh°C	—	—	0.022	0.025	0.022
曲げ弾性率 $\text{kg}/\text{cm}^2$	20,000	32,000	—	—	—

[0112]

[Table 2]

	実施例 6	実施例 7	実施例 8	比較例 1	比較例 2
発泡倍率 (倍)	1.9	1.6	1.3	2.6	1.7
平均気泡径 ( $\mu\text{m}$ )	0.5	0.7	0.4	1.50	1.20
独立気泡率 (%)	—	—	8.6	—	9.3
熱伝導率 Kcal/mh°C	—	—	0.015	—	0.030
曲げ弾性率 $\text{kg}/\text{cm}^2$	38,000	28,000	—	10,000	—

[0113]



[Table 3]

	比较例 3	比较例 4	比较例 5
発泡倍率 (倍)	2.2	1.6	1.5
平均気泡径 ( $\mu\text{m}$ )	100	80	90
独立気泡率 (%)	92	—	—
熱伝導率 $\text{Kcal/mh}^\circ\text{C}$	0.029	—	—
曲げ弾性率 $\text{kg/cm}^2$	—	28,000	21,000

[0114]

[Table 4]

	実施例 9	実施例10	実施例11	実施例12	実施例13
発泡倍率 (倍)	1.2	1.8	3.5	3.0	2.5
平均気泡径 ( $\mu\text{m}$ )	2.0	1.2	8.5	4.9	2.1
独立気泡率 (%)	95	88	100	97	93
熱伝導率 $\text{Kcal/mh}^\circ\text{C}$	0.024	0.022	—	0.023	0.023
曲げ弾性率 $\text{kg/cm}^2$	—	—	35,000	—	—

[0115]

[Table 5]

	実施例14	実施例15	実施例16	実施例17	実施例18
発泡倍率 (倍)	1.5	1.3	3.0	1.6	3.1
平均気泡径 ( $\mu\text{m}$ )	1.1	0.8	7.9	0.5	3.7
独立気泡率 (%)	96	98	86	—	96
熱伝導率 $\text{Kcal/mh}^\circ\text{C}$	0.021	0.024	0.015	—	0.024
曲げ弾性率 $\text{kg/cm}^2$	—	—	—	38,000	—

[0116]

[Table 6]

	実施例19	実施例20	実施例21	実施例22
発泡倍率 (倍)	3.6	6.4	1.7	2.8
平均気泡径 ( $\mu\text{m}$ )	2.2	0.7	1.4	0.8
独立気泡率 (%)	—	98	—	—
熱伝導率 $\text{Kcal/mh}^\circ\text{C}$	—	0.032	—	—
曲げ弾性率 $\text{kg/cm}^2$	28,000	17,000	28,000	22,000

[0117]

[Table 7]

	比较例 6	比较例 7	比较例 8	比较例 9	比较例 10
発泡倍率 (倍)	1.2	1.8	3.3	3.0	1.5
平均気泡径 ( $\mu\text{m}$ )	350	250	150	230	120
独立気泡率 (%)	95	88	100	98	96
熱伝導率 $\text{Kcal/mh}^\circ\text{C}$	0.038	0.033	—	0.028	0.026
曲げ弾性率 $\text{kg/cm}^2$	—	—	26,000	—	—

[0118]

[Table 8]

	比较例11	比较例12	比较例13	比较例14	比较例15
発泡倍率 (倍)	3.0	1.6	3.0	3.8	6.9
平均気泡径 ( $\mu\text{m}$ )	160	80	100	110	90
独立気泡率 (%)	86	—	98	—	98
熱伝導率 $\text{Kcal/mh}^\circ\text{C}$	0.022	—	0.028	—	0.035
曲げ弾性率 $\text{kg/cm}^2$	—	25,000	—	22,000	11,000

[0119]

[Table 9]

	比较例16
発泡倍率 (倍)	2.8
平均気泡径 ( $\mu\text{m}$ )	150
独立気泡率 (%)	—
熱伝導率 $\text{Kcal/mh}^\circ\text{C}$	—
曲げ弾性率 $\text{kg/cm}^2$	12,000

[0120]

[Effect of the Invention]As mentioned above, according to the manufacturing method of an invention of claim 1, the air bubbles formed into foam decompose by irradiating a foaming agent with radiation, it is formed by generating gas, and, moreover, the air bubbles of a small path can be certainly formed compared with the case where the conventional heat decomposition type blowing agent is used. And since it is a thing into which a foaming agent is made to disassemble by the exposure of radiation, since the air bubbles of the above small paths can be formed without needing precise temperature control etc., they can be used conveniently for a mass production.

[0121]Similarly according to the invention according to claim 2, it decomposes by irradiating the above-mentioned radiation, The foam formation generating agent which generates gas is

beforehand mixed to resin with a foaming agent, and since generate the air bubbles of a small path first, a foaming agent is made to disassemble further and the air bubbles of a desired path are formed by emitting radiation, the foam which has desired expansion ratio and the air bubbles of a path can be obtained easily. And since it is a thing into which a foam formation generating agent is made to decompose by the exposure of radiation, Since the path of the air bubbles generated first can be controlled without needing precise temperature control etc., It can control without needing temperature control precise also about the path of the air bubbles eventually formed by operation of a foaming agent etc., and the air bubbles of a path smaller than before can be formed certainly. Therefore, it can use conveniently for a mass production of foam.